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Simulations of Vibrational Relaxation  
in Dense Molecular Fluids

by

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Abstract

In the understanding of high-temperature and -pressure chemistry in explosives, first step is the study of the transfer of energy from translational degrees of freedom into internal vibrations of the molecules. We present new methods using nonequilibrium molecular dynamics (NEMD) for measuring vibrational relaxation in a diatomic fluid, where we expect a classical treatment of many-body collisions to be relevant because of the high densities (2 to 3 times compressed compared to the normal fluid) and high temperatures (2000-4000 K) involved behind detonation waves. NEMD techniques are discussed, including their limitations, and qualitative results presented.

## I. Introduction

The phenomena of energy-sharing among center-of-mass translational degrees of freedom and internal (rotational and vibrational) degrees of freedom in dense, hot molecular fluids are crucial to the understanding of a variety of chemical explosive properties. We shall illustrate, in a highly simplified way, the processes occurring in the passage of a steady detonation wave in a condensed (fluid or solid) high explosive. First, as we sit on some typical explosive (that is, chemically unstable) molecule, a compressive shock wave arrives in the form of collisions from neighboring molecules. Center-of-mass separations shrink, causing the density to rise sharply, along with the "temperature" in the shock propagation direction. The "temperature" in the transverse directions is cold at first, until sideways collisions cause translational kinetic energy in the longitudinal direction to be fed into transverse (shearing) motion. Within one or two mean collision times, all center-of-mass kinetic energies equilibrate, so that in the sense of local equilibrium, we may speak more correctly about temperature. Soon thereafter, rotational motions of the molecules also equilibrate, leaving only internal vibrations of the molecules relatively "cold". If the molecule is fairly complex, there will exist lower-frequency bond-bending modes that are more easily excited than the high-frequency bond-compression modes. The closer two frequencies are, the easier it is for them to "talk" to each other, i.e., to transfer energy; this resonance phenomenon occurs both classically and quantum-mechanically. Thus a sequence of energy transfers will occur, climbing a ladder in the frequency domain: the lowest frequency modes to be equilibrated are translational, followed roughly by rotations, bond-bending, and finally bond-stretching vibrations.

The latter vibrational temperature may take a long time to equilibrate. Our aim is to understand the time (and also, the mechanisms) it takes for energy from a shock front to be transferred into molecules, in order to prepare them for the highly-excited vibrational states necessary for electronic rearrangement (chemical reaction) to occur. Once electronic states are significantly perturbed through vibrations, chemical energy in unstable bonds can be released, which drives the detonation -- in effect, providing the piston for the shock wave. Of course, this is undoubtedly a terribly oversimplified picture of the time-scales in high explosive detonations. (We have said nothing about the effect of inhomogeneities, for example.) Nevertheless, the statistical process of energy transfer from center-of-mass collisions at high density up through the frequency ladder into internal vibrations must be understood before we will have even a rudimentary understanding of the kinetics of explosive chemical reactions.

Because of the high densities involved in this picture of detonations in condensed explosives, we are forced to consider many-body effects -- there are no isolated binary collisions between molecules. Because of the high temperatures involved, we suppose that even if binary collisions were appropriate, the most efficient energy transfer would occur when the relative kinetic energy of a colliding pair of molecules is several times  $kT$ ; therefore, at these temperatures, it is plausible quantum effects on vibrational relaxation are small. The method of molecular dynamics (MD), where the classical many-body problem is solved numerically, is the only tool available for studying vibrational relaxation in dense, hot molecular fluids.

MD has been successfully applied to equilibrium problems. Even though it is intrinsically a time-dependent method, as distinct from Monte Carlo,

where configurations are generated so as to sample from a canonical ensemble. The principal limitation to MD in equilibrium problems has been the smallness of systems considered,  $N \sim 100$ -1000 molecules. At normal fluid densities, such a small sample would not possess properties at all close to bulk values. With the surface skin depth given by the range of interatomic forces, if 100-1000 particles were placed in a box with rigid walls, the walls would demonstrate the results -- everything would be surface; there would be no bulk to speak of. Periodic boundary conditions, where the "box" of  $N$  particles in volume,  $V$ , is surrounded by an infinite periodic array, or checkerboard, of such systems, removes this surface problem to such an extent that corrections to equilibrium properties are of relative order  $1/N$ . In nonequilibrium molecular dynamics (NEMD), where, for example, a fluid is sheared by moving two parallel walls in opposite directions, similar wall, or surface effects are seen. The shear viscosity is given by the shear stress averaged over time, divided by the steady shear rate. If, instead of moving walls, homogeneous external forces are applied to particles throughout the fluid, the resulting shear viscosity (in three dimensions) is noticeably more independent of system size. Thus, both equilibrium and steady-state time averages are reliably obtained by MD or NEMD. What is not as clear, however, is whether truly time-dependent properties, such as a relaxation time (or its inverse, the relaxation rate), can be reliably obtained. In equilibrium systems, fluctuations about equilibrium yield time correlation functions, where the influence of periodic boundary conditions can affect the results for times longer than that for a sound wave to cross the system. In nonequilibrium systems, not only are the correlations between periodic cells of concern, but also the effect upon rates due to external forces must be taken into account. One

of the aims of this paper is to show just how such problems in NEMD can be carefully resolved in order to obtain believable results for nonequilibrium rate processes.

In this paper, we will concentrate on a relatively simple problem. We will study the rate of energy transfer from translational and rotational degrees of freedom into bond vibration in a hot, dense diatomic molecular fluid. We have chosen a potential energy surface (see Appendix) that is a reasonable approximation to nitrogen ( $N_2$ ). In addition to temperature and density, we can vary the bond vibrational frequency to study its effect on the rate of relaxation. Typically, we are concerned with  $N_2$  at 2 to 3 times normal fluid density ( $\sim 2 \text{ g/cm}^3$ ), temperatures of 2000-4000 K, and pressures of 200-300 kbar, that is, states like those achieved behind detonations of high explosives. For the purposes of this study, we will assume and that our idealized diatomic molecular fluid is dense but isotropic, that is, if a shock wave has passed through, the shear stress has been relieved by viscous flow, and that the temperatures in the 3 translational and 2 rotational degrees of freedom have equilibrated to a high value, while the vibrational temperature is at the low ambient value, i.e., room temperature (300 K). The process whereby the temperature in the bond-vibrational and the 5 other "external" modes, or reservoirs, come to equilibrium isoenergetically will be referred to as "adiabatic". The most important issue to be considered in adiabatic relaxation is whether it is correct to suppose that the vibrational temperature  $T_{\text{vib}}$  relaxes exponentially from its cold initial temperature  $T_0$  to the final equilibrium temperature  $T$  with some characteristic relaxation time  $\tau_{\text{vib}}$ :

$$T_{\text{vib}}(t) = T - (T - T_0)\exp(-t/\tau_{\text{vib}}) \quad . \quad (1)$$

The vibrational relaxation rate  $v_{\text{vib}}$  is then obtainable from the initial temperature increase

$$v_{\text{vib}} = \tau_{\text{vib}}^{-1} = \frac{\dot{T}_{\text{vib}}(0)}{T - T_0} \quad (2)$$

Equation (1) can only make sense if the vibrational mode equilibrates with the external reservoir at fixed temperature  $T$ , which in the adiabatic case is both the final temperature and the average, neglecting potential energy redistribution:

$$5T_x(t) + T_{\text{vib}}(t) \cong 6T \quad .$$

One could argue that Eq. (1) is therefore not valid for adiabatic relaxation, since the vibrational reservoir does not equilibrate with itself, even insofar as its contribution to the average temperature  $T$ , but rather with a continuous sequence of external mode temperatures from  $T_x(0)$  down to  $T$ . Equation (2) would then have to be replaced by

$$v_{\text{vib}}[T_x(t)] = \frac{\dot{T}_{\text{vib}}(t)}{T_x(t) - T_{\text{vib}}(t)} \quad , \quad (2a)$$

which describes a complex multi-temperature relaxation process. An unambiguous rate could then be obtained only at  $t = 0$ . (See Fig. 1 for an illustration of totally adiabatic response of the vibrational and external reservoirs.)

Since the adiabatic response gives only the initial rate in a straightforward manner, some of the ambiguity can be eliminated by

thermostatting the external reservoir at temperature  $T_x = T$ , leaving the vibrational temperature to rise to  $T_0$  to  $T$  in a partially adiabatic manner. (See Fig. 2 for an illustration of partial adiabatic response of the vibrational reservoir to a fixed external reservoir temperature.)

a reservoir can be fixed at constant temperature  $T_x = T$  by several means: isokinetic thermostatting (either by Gaussian constrained dynamics<sup>1a,b</sup> or its equivalent for small time-steps, velocity scaling,<sup>1c</sup> to achieve a perfectly constant kinetic energy in the external reservoirs), Andersen stochastic thermostatting<sup>2</sup> (where velocities are randomly reset from a Maxwell-Boltzmann distribution), on Nosé-Hoover feedback thermostatting<sup>3</sup> (where the equation of motion of an extra degree of freedom -- the thermostatting coefficient  $\xi$  -- is included in the dynamics).

By completely thermostatting the vibrational degree of freedom at the low temperature  $T_0$  and the other degrees of freedom at the high temperature  $T$ , we eliminate the ambiguities of multitemperature rates mentioned above, and the problem is reduced to measuring  $\dot{T}_{vib}(0)$  in Eq. (2) as a time average of the appropriate quantities, depending on thermostatting mechanisms, over long enough times in a steady-state nonequilibrium system. In the following sections, we will discuss each of the methods outlined above and present results for our idealized dense, hot molecular fluid.

We can already point out some qualitative features of vibrational relaxation in these systems: the rate  $\nu_{vib}$  decreases exponentially with the vibrational  $\omega_e$  of the bond,  $\nu_{vib}$  increases faster than linearly with density;  $\nu_{vib}$  increases with temperature qualitatively like an Arrhenius law, namely an exponential of minus the inverse temperature. We emphasize that our interest is in dense, hot fluids where we suppose that quantum effects



are small (that is, the collisional velocities that transfer energy most efficiently correspond to several times  $kT$ , or in other words, sample the wings of the Maxwell-Boltzmann velocity distribution) and that isolated binary collisions are inappropriate at these high densities to account for the relaxation phenomenon. Nevertheless, the techniques developed here may be applicable in other regimes as well. Finally, we show that the Nosé-Hoover thermostat possesses superior characteristics for measuring rate processes, including the capability of extrapolating out its effect altogether, compared to Andersen's stochastic thermostat or the Gaussian isokinetic thermostat.

## II. Methods

In this section we describe the NEMD methods we have developed for studying vibrational relaxation. First, the common element to all these approaches is the absolute necessity for transforming from the six cartesian atomic coordinates  $(\vec{r}_1, \vec{r}_2)$  of each diatomic molecule to three center-of-mass  $(\vec{R})$  and relative  $(\vec{r})$  molecular coordinates:

$$M\vec{R} = m_1\vec{r}_1 + m_2\vec{r}_2 \quad ,$$

$$\vec{r} = \vec{r}_2 - \vec{r}_1 \quad ,$$

where the atomic masses  $(m_1, m_2)$  are related to the total molecular mass by  $M = m_1 + m_2$  and to the reduced mass by  $\mu = m_1 m_2 / M$ . The kinetic energy of the system can then be partitioned into  $3(N-1)$  translational (total linear momentum  $N\vec{p}_0 = \sum \vec{p} = 0$ ),  $2N$  rotational, and  $N$  vibrational degrees of freedom:

$$\begin{aligned}
 K &= \sum_{i=1}^N \sum_{a=1}^2 \frac{1}{2} m_a |\dot{r}_{ia}|^2 \\
 &= \sum_{i=1}^N \frac{1}{2} M |\dot{\mathbf{R}}_i|^2 + \frac{1}{2} \mu |\dot{\mathbf{r}}_i|^2 \\
 &= K_{\text{trans}} + K_{\text{rot}} + K_{\text{vib}} \quad ,
 \end{aligned}$$

where in the thermostatted steady state the time averages  $\langle \dots \rangle_{ss}$  of kinetic energies are related to the temperatures by

$$\langle K_{\text{trans}} \rangle_{ss} = \frac{3}{2} (N - 1) kT \quad ,$$

$$\langle K_{\text{rot}} \rangle_{ss} = N kT \quad ,$$

$$\langle K_{\text{vib}} \rangle_{ss} = \frac{1}{2} N k T_0 \quad .$$

It is essential to partition kinetic energy into these natural molecular reservoirs in order to thermostat the vibrational temperature at the lower value  $T_0$  and the external temperatures (translational and rotational) at the higher value  $T$ . The atomic cartesian reservoirs simply will not control the temperatures, even for the relatively simple case  $T_0 = T$ ; the vibrational temperature for reasonable bond force constants (much larger than intermolecular) stubbornly refuses to equilibrate. The center-of-mass and relative forces (dropping molecular index  $i$ ) are then

$$\vec{F} = M\ddot{\vec{R}} = m_1\ddot{\vec{r}}_1 + m_2\ddot{\vec{r}}_2 = \vec{F}_1 + \vec{F}_2 \quad ,$$

$$\vec{f} = \mu\ddot{\vec{r}} = \frac{m_1}{M} m_2\ddot{\vec{r}}_2 - \frac{m_2}{M} m_1\ddot{\vec{r}}_1 = \frac{m_1}{M} \vec{F}_2 - \frac{m_2}{M} \vec{F}_1 \quad .$$

The relative velocities and forces can be further decomposed into components parallel and perpendicular to the bond, where the unit vector along the bond is  $\hat{r} = \vec{r}/|\vec{r}|$ , e.g.,

$$\dot{\vec{r}} = (\dot{\vec{r}} \cdot \hat{r})\hat{r} \quad ,$$

$$\dot{\vec{r}} = \dot{\vec{r}} + \dot{\vec{r}} \quad ,$$

the vibrational and rotational velocities, respectively.

The thermostatted equations of motion for each reservoir can be written in the form:

$$\dot{q} = \frac{p}{m} \quad ,$$

$$\dot{p} = F - \xi p \quad , \tag{3}$$

where the coordinate is  $q$  and momentum is  $p$ ;  $F$  is the force, which in our model is assumed to arise from atom-atom intermolecular interactions plus an atom-atom bond potential (see Appendix for details). The thermostating coefficient  $\xi$  is related to the relaxation rate  $\nu_{\text{vib}}$  ( $=\tau_{\text{vib}}^{-1}$ ) by noting that

$$\begin{aligned}
\dot{K} &= \sum_m \frac{p}{m} p \\
&= \sum_m \frac{p}{m} (F - \xi p) \\
&= \sum Fq - 2K\xi \quad . \quad (4)
\end{aligned}$$

At the thermostatted steady state

$$\begin{aligned}
\langle \dot{K} \rangle_{ss} &= 0 = \langle \sum Fq \rangle_{ss} - 2\langle K\xi \rangle_{ss} \\
&= \langle \dot{K}(0) \rangle_{ss} - 2K_0 \langle \xi \rangle_{ss} \quad ,
\end{aligned}$$

where we have made the identification that the initial adiabatic ( $\xi \equiv 0$ ) rate is

$$\dot{K}(0) = \sum Fq = \frac{1}{2} g k \dot{T}(0)$$

(g is the number of degrees of freedom, e.g.,  $g = N$  = number of molecules for vibration), so that

$$\langle \dot{K}(0) \rangle_{ss} = \langle Fq \rangle_{ss} \quad .$$

Then,

$$\langle \dot{T}(0) \rangle_{ss} = 2T_0 \langle \xi \rangle_{ss} \quad ,$$

which, with Eq. (2) gives

$$\nu_{\text{vib}} = \frac{2\langle \xi_{\text{vib}} \rangle_{\text{us}}}{\frac{T}{T_0} - 1}$$

We use this equation for both the Gaussian isokinetic and Nosé-Hoover isothermal methods. The physical interpretation is that for the lower vibrational temperature  $T_0 < T$ , the thermostating coefficient is positive,  $\langle \xi \rangle_{\text{ss}} > 0$ . Collisions tend to drive the vibrational kinetic energy up, on the average,  $\langle F\dot{q} \rangle > 0$ , while the thermostat bleeds vibrational kinetic energy away, much like linear viscous damping. Of course, the small systems we study have large fluctuations, so that at times,  $\xi$  behaves like viscous "undamping." Thermostating is essential, even for preparing the initial state for adiabatic response methods, but we begin by discussing adiabatic relaxation methods, followed by the isokinetic method of thermostating, Andersen stochastic thermostating, and finally Nosé-Hoover feedback thermostating.

#### IIA. Adiabatic Relaxation

The method for measuring adiabatic relaxation is to select a state from a constrained nonequilibrium simulation, as described in the next three sub - sections for example, as an initial condition for standard MD (Newton's equations of motion). With the thermostating constraints entirely removed, so that the vibrational temperature can rise to  $T$  from  $T_0$  and the external temperature can drop to  $T$  from  $T_x$ , the typical adiabatic response is shown in Fig. 3. Also shown is the difference in response that occurs when only the vibrational thermostat is turned off (labeled partial in Fig. 3). The partial adiabatic realization was obtained, as was the

former, from a Nosé-Hoover NEMD experiment (see Sec. IID) with thermostating rates  $\nu_T t_0 = 10$  in the external reservoirs as well as in the vibrational mode; the external reservoir temperature was set and maintained at  $T_x = 4000$  K while the vibrational temperature was set at  $T_0 = 300$  K; at the beginning of the partial adiabatic run, only the vibrational thermostating rate was set to zero, while in the total adiabatic run, all thermostating was turned off.

Initially, for both realizations, the vibrational temperature is identical, with detectable differences appearing after  $0.1 - 0.2 t_0$ . After approximately one relaxation time, the partial adiabatic response has clearly risen well beyond the fluctuation level above the total adiabatic response, the latter having slowed down by virtue of the drop in the external temperature (initially,  $T_x = 4000$  K, finally  $T = 3400$  K). If the vibrational relaxation rate exhibits an Arrhenius behavior appropriate to a thermal activation mechanism,

$$\nu_{\text{vib}}(T_x) = \nu_{\text{vib}}(\infty) e^{-\theta/T_x},$$

where  $T_x$  is the external temperature, then the difference in the two curves in Fig. 5 can be reconciled if the activation temperature  $\theta$  is roughly 18,000 K and the vibrational relaxation in the partial adiabatic case is simple exponential (no dependence on  $T_{\text{vib}}$ ). This estimate is a reasonable one in view of a body of calculations we have done at different temperatures. Thus we can answer the question,  $\nu_{\text{vib}}$  is a function of what temperature? -- the external temperature (translation and rotation).

The main practical difficulty of measuring the vibrational relaxation rate by the partial adiabatic method, which, at least, is a one-temperature process as we have just seen, is illustrated in Fig. 4. The two curves

shown differ only in the initial phase, chosen from a Nosé-Hoover thermostatted run: in one case, the vibrational thermostat was turned off at  $t = 40 t_0$ ; in the second,  $t = 39 t_0$ . It is clear that one must average over an ensemble of starting times in order to sort out the considerable effects of fluctuations on the measured rate of vibrational relaxation. Even the curvatures of these two traces are different, the latter being steeper. We are thus led to the thermostatted methods of the following subsections for reliable measurements. The motivation for these methods is to replace an ensemble average over starting points with a time average over a continuously-restarted steady-state experiment.

#### IIB. Isokinetic Thermostatting

There are two forms of isokinetic thermostatting, where the kinetic energies of each of the reservoirs -- translational, rotational, and vibrational -- are kept constant. Historically, the first method to appear was velocity scaling<sup>1c</sup>. In finite central difference form. Newton's equations of motion are written

$$\Delta q_+ = \Delta q_- + F \Delta t^2 / m \quad ,$$

with displacements evaluated halfway between time steps  $\Delta q_{\pm} = \Delta q(t \pm \frac{1}{2} \Delta t)$  and the coordinates given by  $q(t + \Delta t) = q(t) + \Delta q(t + \frac{1}{2} \Delta t)$ ; the force is evaluated at time  $t$ . In velocity rescaling, the displacement  $\Delta q_+$  is scaled so as to fix the total kinetic energy for a given reservoir:

$$\Delta q_+ = \alpha \Delta q_+ \quad ,$$

where  $\alpha$  is the velocity scaling factor. At time  $t + \frac{1}{2} \Delta t$ , the kinetic energy is equal to the preset value  $K_0$ , just as it was at time  $t - \frac{1}{2} \Delta t$ :

$$\begin{aligned}
K &= \sum \frac{1}{2} m \frac{\Delta \dot{q}^2}{\Delta t} \\
&= \alpha^2 \sum \frac{1}{2} m \frac{\Delta q^2}{\Delta t^2} \\
&= \alpha^2 \sum \frac{1}{2} m \frac{\Delta q_-^2}{\Delta t^2} + \sum F \Delta q_- + \dots \\
&= \alpha^2 (K_0 + \sum F \Delta q_- + \dots) \\
&= K_0 \quad ,
\end{aligned}$$

whence

$$\begin{aligned}
\alpha &= 1 - \frac{\sum F \Delta q_-}{2K_0} + \dots \\
&= 1 - \Delta t \frac{\sum F \dot{q}_-}{2K_0} + \dots \quad ,
\end{aligned}$$

The Gaussian feedback equations of motion<sup>1a,b</sup> are embodied in Eq. (3).

In finite difference form, with  $\dot{q}(t) = \Delta q / \Delta t$  and  $\Delta q = \frac{1}{2}(\Delta q_+ + \Delta q_-)$ :

$$\begin{aligned}
\Delta q &= \Delta q + F \Delta t^2 / m - \xi \Delta q \Delta t \\
+ &\quad -
\end{aligned}$$



$$= \frac{(1 - \frac{1}{2} \xi \Delta t) \Delta q + F \Delta t^2 / m}{1 + \frac{1}{2} \xi \Delta t} \quad (6)$$

Since  $K = K_0$  is the fixed value of the kinetic energy, we may set  $\dot{K} = 0$  in Eq. (4) to get the thermostating coefficient

$$\xi_G = \frac{\Sigma F \dot{q}}{2K_0}$$

Clearly, for small time steps, the Gaussian feedback and velocity scaling methods are identical, with the velocity scaling factor given by  $\alpha = 1 - \xi_G \Delta t + \dots$ . Since velocity scaling is a somewhat simpler scheme to implement, we evaluate the vibrational relaxation rate by the equivalent form of Eq. (5):

$$v_{\text{vib}} = \frac{\alpha^{-2} - 1}{\Delta t (T/T_0 - 1)}$$

The adiabatic methods for our small ( $N=108$ ) systems are quite noisy, as we have seen in the last subsection, but the isokinetic rate as computed from the above equation is almost a factor of two higher. The flaw in the isokinetic thermostating method is that it is impossible to separate out the effects of thermostating on rate processes. That is, the measured rate of vibrational relaxation could very well be the sum of two terms: the underlying, unthermostatted (adiabatic) rate, plus a contribution from the thermostating process itself. The homogeneous intrusion into the dynamics, small though it may be, alters the velocity distribution function. If the alteration affects the high-velocity wings of the

distribution (as it most surely does), then the rate is also affected, since high-velocity collisions the most efficient means of energy transfer. The following thermostating schemes have this same limitation, but their degree of intrusion into the usual dynamics can be varied, unlike the isokinetic methods.

### IIC. Andersen Stochastic Thermostating

In a landmark paper, Andersen<sup>2</sup> showed how velocities in MD could be altered in a stochastic way, so that time averages along an equilibrium "trajectory" give the same values as the canonical (NVT) ensemble, rather than the usual MD ensemble (NVE,  $N\vec{p}_0 = 0$ ) values. The stochastic prescription is to select particles at random at a thermostating rate  $\nu_T = 1/\tau_T$ , such that a fraction of particles  $\nu_T \Delta t = \Delta N/N$  per time step  $\Delta t$  have their velocities reset from a Maxwell-Boltzmann velocity distribution with temperature  $T_0$ ; i. e., if random number  $i$  ( $i = 1, 2, \dots, N$ ) uniformly distributed between 0 and 1 satisfies  $i/\tau_T < \Delta t$ , then reset the displacement by the Box-Muller transformation<sup>4</sup> (uniform - to Gaussian-distributed random variables)

$$\cos 2\pi ''$$

$$\Delta q_i' = \lambda (-\ln \xi')^{\frac{1}{2}}.$$

$$\sin 2\pi '' ,$$

where  $\xi'$  and  $\xi''$  are a pair of random numbers uniform on the interval  $[0,1]$  and  $\lambda = \Delta t (2kT_0/m)^{\frac{1}{2}}$  ensures that the long-time average of  $K$  is  $\frac{1}{2} N k T_0$ :

$$\begin{aligned}
\langle K \rangle &= \sum \frac{1}{2} m \frac{\langle \Delta q_i^2 \rangle}{\Delta t^2} \\
&= g \cdot \frac{m\lambda}{2\Delta t^2} \langle -\ln \rangle \cdot \frac{1}{2} \langle \cos^2 2\pi'' + \sin^2 2\pi'' \rangle \\
&= \frac{1}{2} g k T_0,
\end{aligned}$$

since  $\langle -\ln \rangle = 1$ .

There are three serious objections to this method of thermostating. First, if the rate of thermostating  $\nu_T$  far exceeds any natural rates, such as the collision rate, particles will simply jiggle furiously about their current positions, diffusing very slowly in configuration space, while executing the expected canonical fluctuations in momentum space. Since all of phase space must be accessible at equilibrium, it will take a very long time to obtain canonical ensemble averages as trajectory time averages in the limit  $\nu_T \rightarrow \infty$ . Second, if  $\nu_T$  is too slow compared to the collision rate, an inordinate amount of time may be spent waiting for momentum-space transients to settle down, especially in the nonequilibrium case. Even though Andersen proved that his procedure would give correct canonical ensemble results, he did not guarantee that it could be done in less than infinite time -- an explicit statement of ergodicity problems in the either limit  $\nu_T \rightarrow 0$  or  $\nu_T \rightarrow \infty$ . The infinite time required to achieve either equilibrium or a nonequilibrium steady state is a serious practical limitation. These ergodicity difficulties can be overcome by choosing  $\nu_T$  to be not too far from the collision rate, avoiding both  $\nu_T = 0$  and  $\nu_T = \infty$  limits.

The third, and perhaps most serious objection to the Andersen thermostatting procedure is illustrated in Fig. 5. In a nonequilibrium experiment, the Andersen thermostat fails to maintain the vibrational temperature at its preset value  $T_0$ . (Berendsen's deterministic scheme<sup>5</sup> also has this shortcoming.) The problem is not simply one of waiting long enough for a transient to settle down, since the temperature has fairly quickly (i.e., on the order of  $\tau_T$ ) reached a steady state value  $T_0' > T_0$ . The relaxation rate  $v_{vib}(T, v_T)$  is given then by

$$\frac{1}{2} gk(T - T_0') v_{vib} = \dot{K}_{vib}(0)_{ss} = \frac{\langle \Delta K_{vib} \rangle_{ss}}{\Delta t},$$

where  $\Delta K_{vib} = \sum \frac{1}{2} \mu (\Delta q_i^2 - \Delta q_i'^2) / \Delta t^2$  is the change in kinetic energy due to resetting the displacements from  $\Delta q_i$  to  $\Delta q_i'$ . However, if higher-order effects make  $v_{vib}$  also dependent upon  $T_0'$  in this example, or if one had hoped to characterize the nonequilibrium steady state before, rather than after the fact, then the Andersen thermostat is inadequate to the task. In the next subsection, we present a deterministic (feedback) method which overcomes this last objection.

#### IID. The Nosé-Hoover Thermostat

Following Andersen's work, Nosé<sup>3a</sup> derived a deterministic method of generating isothermal trajectories. He proposed a Hamiltonian internal energy function involving an extra coordinate and conjugate momentum, whereby time averages over the remaining coordinates and momenta (those of the usual  $N$ -molecule many-body system) yield canonical-ensemble averages and fluctuations. In a further simplification, Hoover<sup>3b</sup> showed that only a single extra variable, the thermostatting coefficient  $\xi$  that appears in the equations of motion [Eq. (3)], is necessary, along with the assumption

of a canonical distribution function and its stationarity at equilibrium. The resulting equation of motion for  $\xi$  is then shown to be:

$$\dot{\xi} = v_T^2 (K/K_0 - 1) \quad (7)$$

The thermostating rate is  $v_T$ , analogous to the Andersen stochastic procedure. We have already derived an expression for the vibrational relaxation rate, given the steady-state nonequilibrium value of  $\xi_{\text{vib}}$ , namely Eq. (5).

It is clear from Eq. (7) that at the steady state  $\langle \dot{\xi}_{\text{vib}} \rangle_{\text{ss}} = 0$ , so that  $\langle K_{\text{vib}} \rangle_{\text{ss}} = K_0$ . In other words, the deterministic thermostat of Nosé and Hoover is able to maintain the temperature at its preset value. This is illustrated in Fig. 6 for a situation very closely parallel to the example of the Andersen thermostat in Fig. 5. Note that when the thermostating time constant has been switched from  $\tau_T = 0.1$  to 0.5 at  $t = 0$ , there is a transient response that settles out in a few times  $\tau_T$ .

Again, as in the Andersen method, the limits  $v_T \rightarrow 0$  or  $v_T \rightarrow \infty$  pose ergodic hazards to the computation of the vibration relaxation time by this homogeneous method. Spurious results can be obtained when the thermalization rate is too much higher than collision frequencies ( $v_T \rightarrow \infty$ ).<sup>6</sup> At the other extreme, one must average over very long times, both to be sure that transients have died out and to compensate for larger fluctuations in  $\xi$ : at equilibrium since  $\xi$  is Gaussian-distributed, one can show that  $\langle \xi^2 \rangle - \langle \xi \rangle^2 = 1/g\tau_T^2$ . This is also true, to a good approximation, away from equilibrium, where  $\langle \xi \rangle \neq 0$ . Nevertheless, over a certain range of thermostating rates, we expect that the vibrational relaxation rate determined by our method can be represented by a linear relation:

$$v_{\text{vib}}(v_T) \approx v_{\text{vib}}(0) + \alpha v_T \quad . \quad (8)$$

That means that the effect of the thermostat on the intrinsic rate process can be extrapolated away.

### III. Results

In the previous section, we have presented some qualitative results for each of the NEMD methods presented. In this section, we compare methods and use them to discuss certain physical features of vibrational relaxation in dense molecular fluids.

In Fig. 7, we show the dependence of the vibrational relaxation rate on thermostating rate for the Andersen stochastic and Nosé-Hoover deterministic thermostating schemes. Also shown at zero thermostating rate are the results for adiabatic response and Gaussian isothermal methods (of course, the latter is really an infinite-rate rather than zero-rate procedure). Notice that, in agreement with Eq. (8), both Andersen and Nosé-Hoover appear to extrapolate to the same value of vibrational relaxation rate in the adiabatic (zero thermostating rate) limit, though the slopes differ dramatically, with the slope in the Andersen method 40 times that of the almost-flat Nosé-Hoover method. The reason for this dramatic difference in slopes is almost surely due to the difference in smoothness of the trajectories: the Andersen method arbitrarily and abruptly resets velocities, often as not ramming molecules into one another in a way inherently far less gentle than the gradual effect of feedback in the Nosé-Hoover method. It is nevertheless comforting that the two methods give the same adiabatic limit, since at least at equilibrium they generate the same long-time averages, namely, canonical averages. This limiting

value is somewhat above the two adiabatic NEMD results; however, it is doubtful that the discrepancy is statistically significant. In order to convince oneself of the significance, an ensemble of adiabatic experiments, rather than only two, would need to be performed. The Gaussian isokinetic result is, however, significantly higher than the adiabatic experiments, by almost a factor of two, and is also higher than any of the Nosé-Hoover realizations, as might be supposed from the relative "stiffness" of the two feedback methods. That is, the Gaussian method rigidly clamps the kinetic energy at a fixed value, with no fluctuations allowed, while the Nosé-Hoover method allows the value to fluctuate about the set value for characteristic times of the order of the thermostating time constant. Nevertheless, the Gaussian method, being deterministic, is gentler than the stochastic method and gives a lower measured vibrational relaxation rate than the Andersen procedure.

These results demonstrate that the Nosé-Hoover method gives essentially the adiabatic vibrational relaxation rate without need for extrapolation to zero thermostating rate, while it is absolutely essential to perform such an extrapolation with the Andersen procedure. The Gaussian method, on the other hand, affords no clue as to the underlying adiabatic rate except to overestimate it. As long as the Nosé-Hoover thermostating rate is neither large compared to the vibrational frequency, nor too small compared to the collision frequency, it is the method of choice among the thermostating procedures presented here. The total adiabatic response method gives a rate that decays with temperature, so that its main utility is to show that the one-temperature partial adiabatic method gives the correct initial rate. Unfortunately, the severe dependence on initial conditions for these small systems ( $N = 108$  molecules), makes it necessary

to perform an impractically large ensemble of partial adiabatic experiments in order to glean the true adiabatic vibrational relaxation rate by this NEMD method. It is comforting to note (at these densities at least) that the results for  $N = 32$  are not noticeably different.

In the remainder of this paper, we will discuss the qualitative features obtained from several adiabatic response experiments. As indicated above, the absolute values of relaxation rates may be suspect, but the trends we will point out are nevertheless valid. First of all, our calculations indicate that the rate of vibrational relaxation drops exponentially as the frequency  $\omega_e$  of the bond vibration increases. For example, at the state point examined in the previous examples ( $\rho = 2.3 \text{ g/cm}^3$ ,  $T = 4000 \text{ K}$ ,  $T_0 = 300 \text{ K}$ ), the rate for  $\omega_e = 322 \text{ THz}$  was  $\sim 0.05 \text{ t}_0^{-1}$ , while at  $\omega_e = 444 \text{ THz}$  (appropriate to  $\text{N}_2$ ) the rate is an order of magnitude smaller. This exponential dependence of energy transfer upon frequency is typical of resonance phenomena. Second, the temperature dependence of vibrational relaxation is approximately Arrhenius. This is not to say that the rate is sufficiently accurate to rule out a Landau-Teller<sup>7</sup> [ $\exp(-\theta/T)^{1/3}$ ] or some other prediction of temperature dependence. Third, the density dependence of the Arrhenius activation temperature is well-approximated by a quadratic function of inverse density. The density dependence is far from linear, that is, isolated binary collisions provide an inadequate description of vibrational relaxation in dense molecular fluids. In future publications, more details of numerical results will be presented.

#### IV. Conclusions

Vibrational relaxation in dense molecular fluids can be best studied by homogeneously-thermostatted nonequilibrium molecular dynamics, using the deterministic Nosé-Hoover equations of motion. For thermostating rates



lower than the collision rate, the intrusion of the thermostat on vibrational relaxation rates is linear. Andersen's stochastic method of thermostating, like the Nosé-Hoover method, allows one to extrapolate away the effects of thermostating upon nonequilibrium rate processes, though the stochastic intrusion is much more dramatic but Andersen's method does not maintain the temperature at a predetermined value. Gaussian isokinetic thermostating is not useful for determining vibrational relaxation rates, since there is no straightforward way to separate out the effects of thermostating. For small systems that are practical for molecular dynamics studies, total adiabatic relaxation is complicated by the fact that the rate is temperature-, and therefore time-dependent. When all but the vibrational temperature is thermostatted (partial adiabatic relaxation), the rate is time-independent, but difficult to measure because of the inherent noisiness (fluctuations) and strong dependence on initial conditions in these small systems. Qualitative features of vibrational relaxation in dense molecular fluids, to be described in more detail in future work, have nevertheless been pin-pointed, namely, the exponential dependence of rate on vibrational frequency, the nonlinearity of the density dependence, and the approximate Arrhenius behavior, suggesting a thermally activated mechanism.

### Appendix: Potentials

The potential energy of the system of N molecules is assumed to be represented by

$$\Phi = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} \sum_{a=1}^2 \sum_{b=1}^2 \phi_{ab}(r_{ia,jb}) + \sum_{i=1}^N \phi(r_{i1,i2}) ,$$

where

$$r_{ia,jb} = |\vec{r}_{ia} - \vec{r}_{jb}|$$

are atom-atom distances,  $\phi_{ab}$  is the unbonded atom-atom intermolecular potential of the exponential-six form

$$\phi_{ab}(r) = \frac{\epsilon}{\alpha-6} \{ 6 \exp[\alpha(1-\frac{r}{r_0})] - \alpha(\frac{r_0}{r})^6 \} ,$$

with  $\epsilon/k = 27.28$  K,  $r_0 = 3.842$  Å, and  $\alpha = 13.16$  (these parameters fit configuration interaction calculations<sup>8</sup> for  $N_2$ , except that  $\epsilon$  is scaled by 0.8 so as to fit experimental shock-wave data; the equilibrium bond length is  $r_e = 1.098$  Å), and  $\phi$  is the intramolecular (bond) potential of the Morse form

$$\phi(r) = D_e \{ 1 - \exp[\xi(1 - \frac{r}{r_e})] \}^2 ,$$

with  $D_e/k = 114,950$  K and  $\xi = 2.952$  (these parameters fit spectroscopic data<sup>9</sup> for  $N_2$ ). By varying  $D_e$  and fixing  $r_e$  and  $\xi$ , we are able to alter the effective frequency of the bond from the  $N_2$  value  $\omega_e = 444$  THz by the relation ( $\mu = 7.00335$  amu is the  $N_2$  reduced mass).

$$\omega_e = (2D_e \xi^2 / \mu r_e^2)^{1/2} .$$

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### Figure Captions

Figure 1. Total adiabatic response of the vibrational temperature  $T_{\text{vib}}$  as a function of time  $t$ . The external degrees of freedom begin the equilibration having been thermostatted at a high temperature  $T_{\text{xy}}$ , while the vibrational degree of freedom has been thermostatted at a low temperature  $T_0$ . At  $t = 0$ , thermostating is stopped and all degrees of freedom relax toward the final temperature  $T$ , where  $6T \sim 5T_{\text{x}} + T_0$ . The initial relaxation time  $T_{\text{vib}}$  is shown.

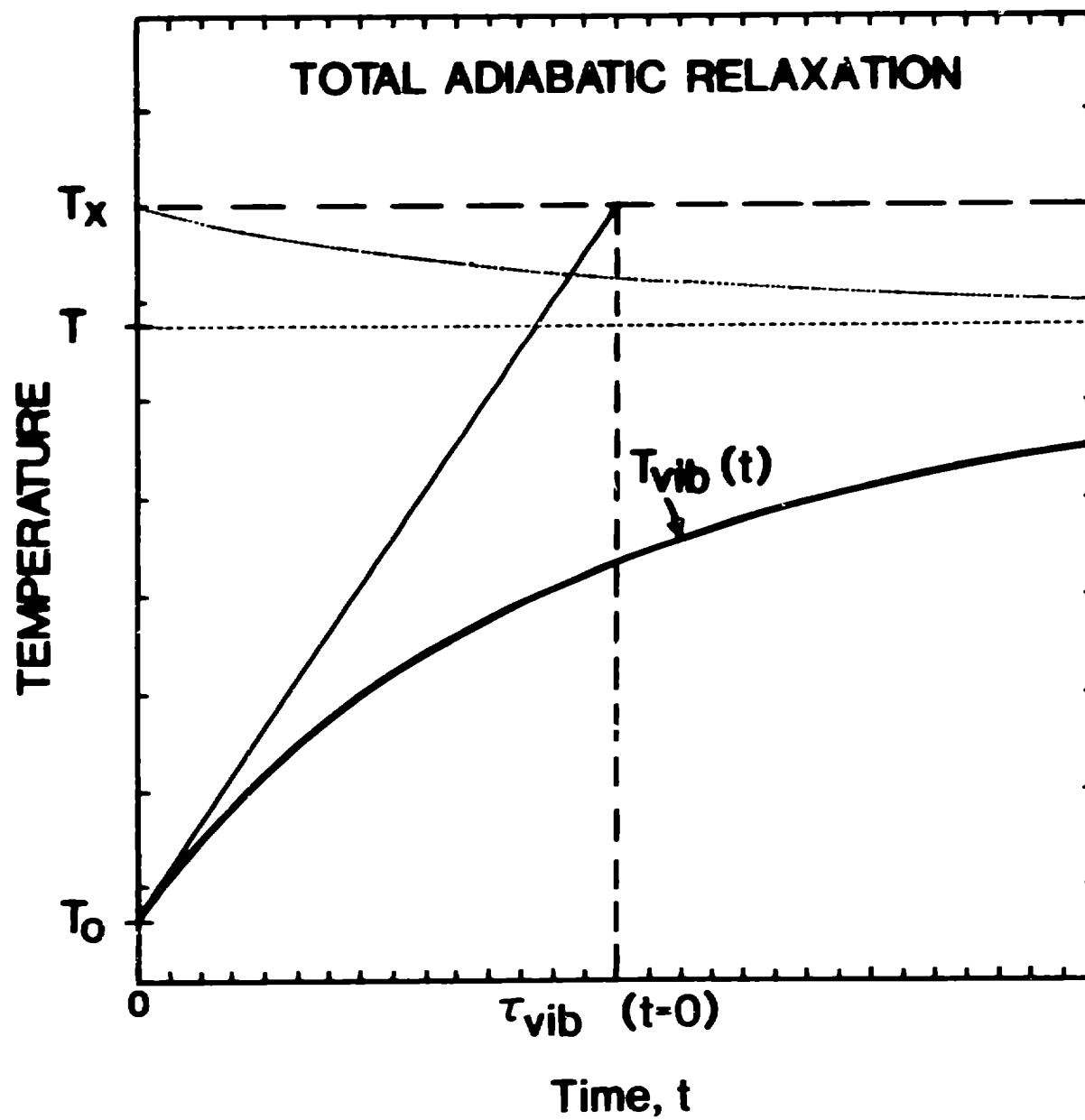
Figure 2. Partial adiabatic response shown as exponential vibrations relaxation process,  $T_{\text{vib}}(t)$ . (See Equation 1 in text). The external degrees of freedom continue to be thermostatted with the vibrational thermostat turned off at  $t = 0$  (compare with Figure 1).

Figure 3. Adiabatic relaxation from the thermostatted initial state: partial, i.e., translation and rotation thermostatted (-); total i.e., no thermostating (---). Fluctuations have been  $t/t_0$  reduced by coarse-graining into bins of  $20\Delta t$  ( $\Delta t = 0.0025 t_0$ ).

Figure 4. Difference in partial diabatic relaxation due to initial conditions: initial phase chosen from Nose-Hoover run at  $t = 40 t_0$  (-); initial phase at  $t = 39 t_0$  (---). Fluctuations reduced by coarse graining (see Figure 5).

Figure 5. Inability of the Andersen thermostat to fix the vibrational temperature  $T_0 = 300 \text{ K}$  ( $T_{\text{trans}} = T_{\text{rot}} = 4000 \text{ K}$ ) in a nonequilibrium simulation ( $\tau_t = \nu_t^{-1} = 0.5 t_0$ ).

FIG. 1



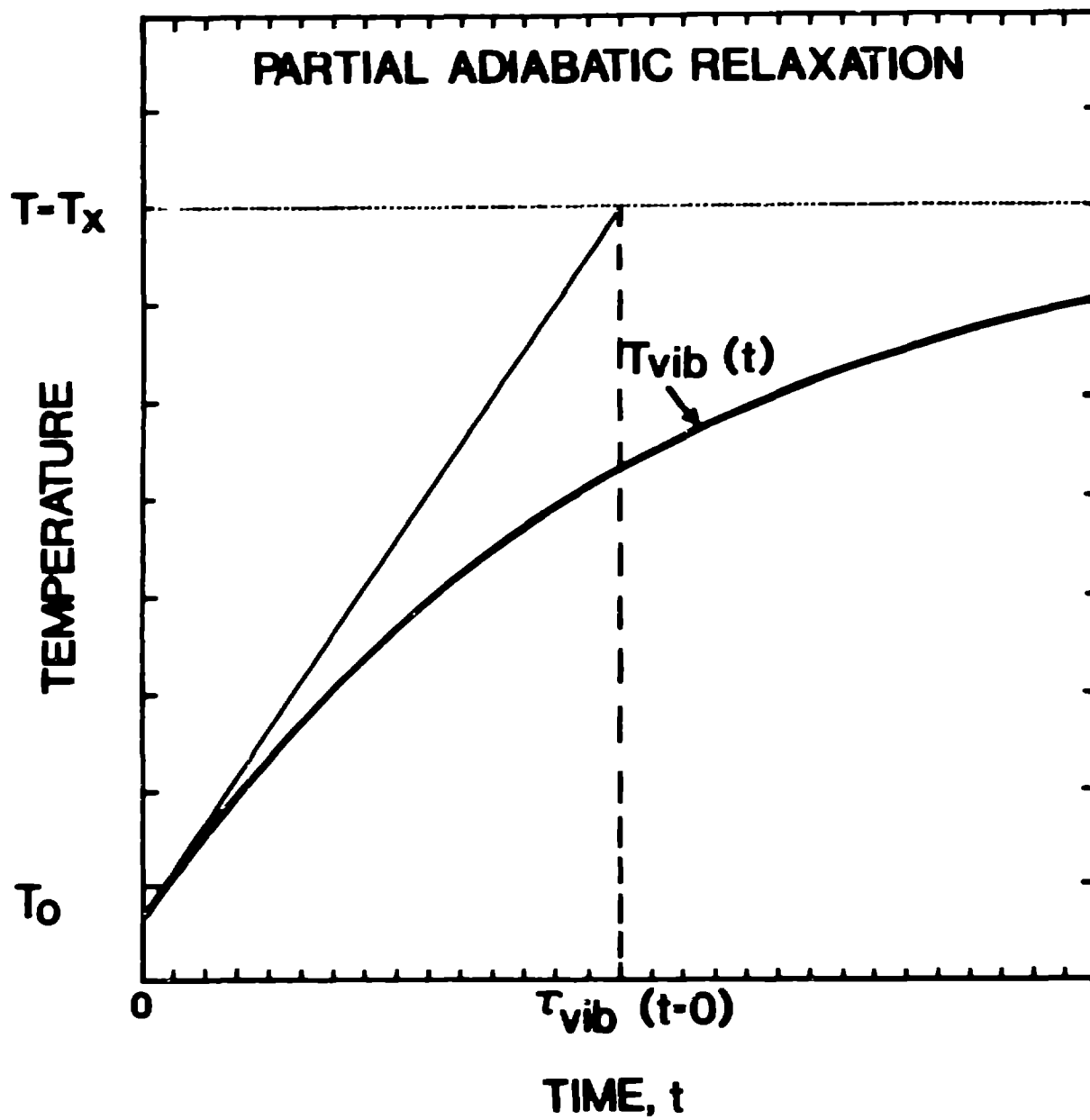


FIG. 2

FIG. 3

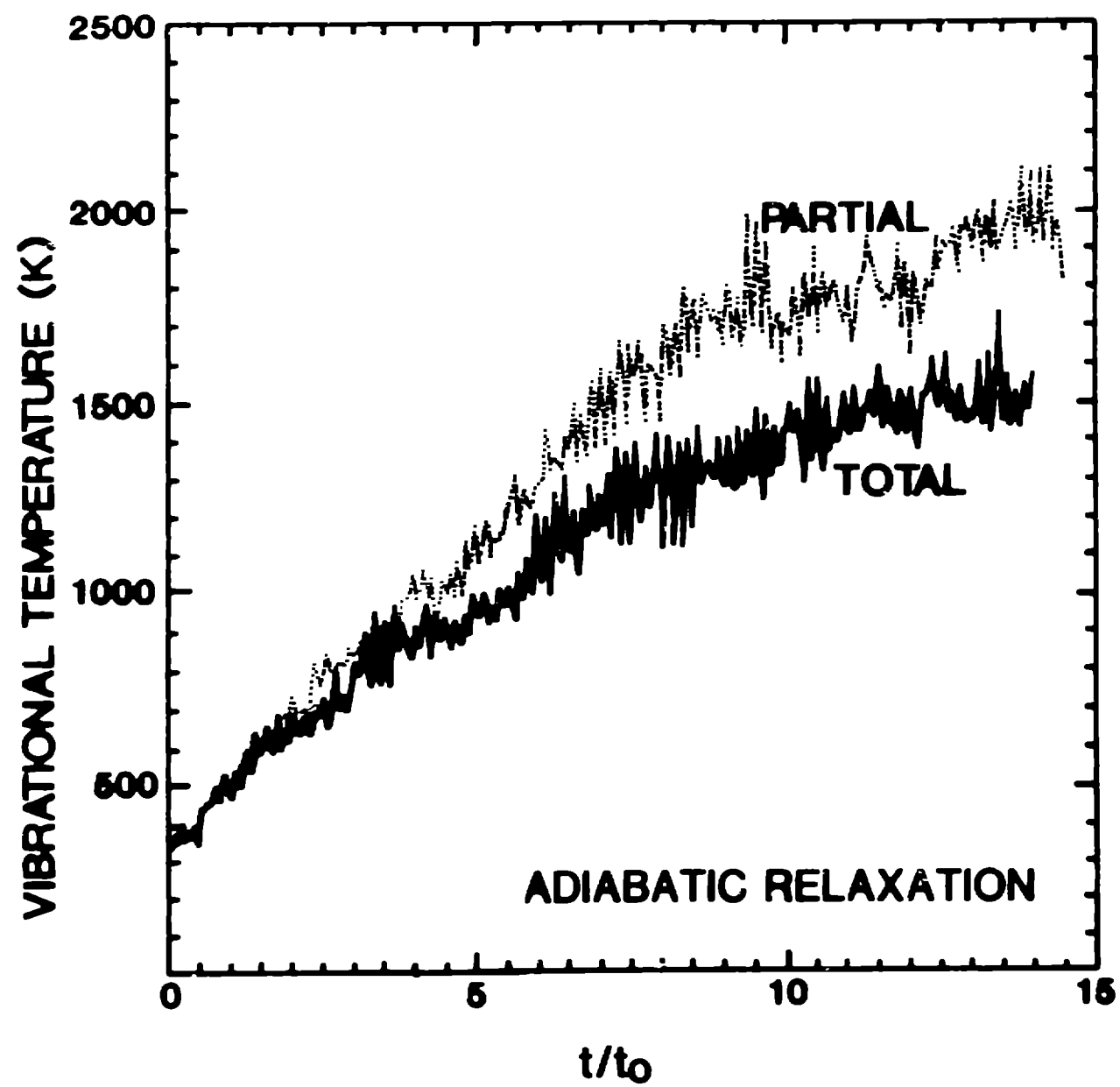


FIG. 4

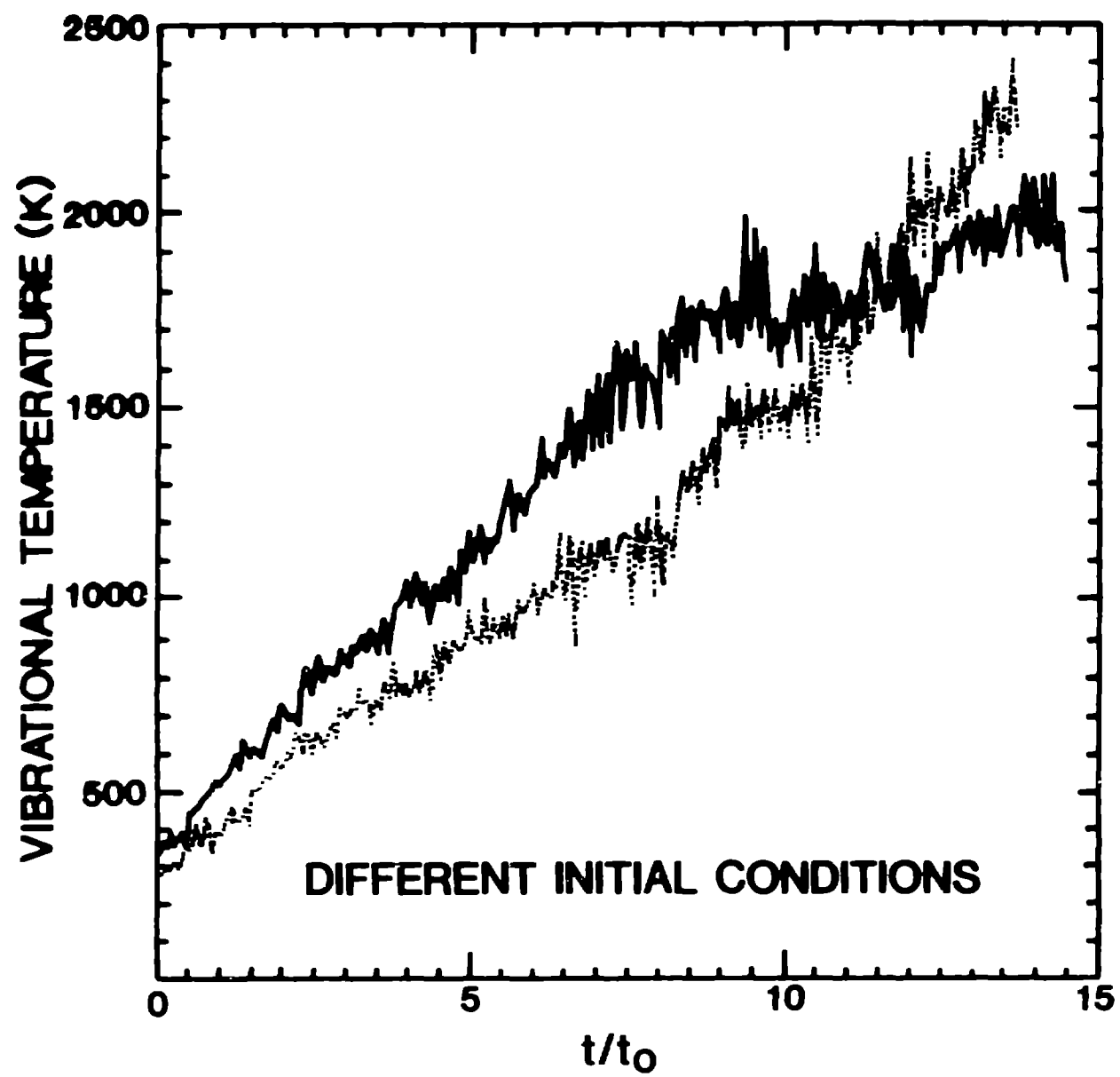




Fig 5

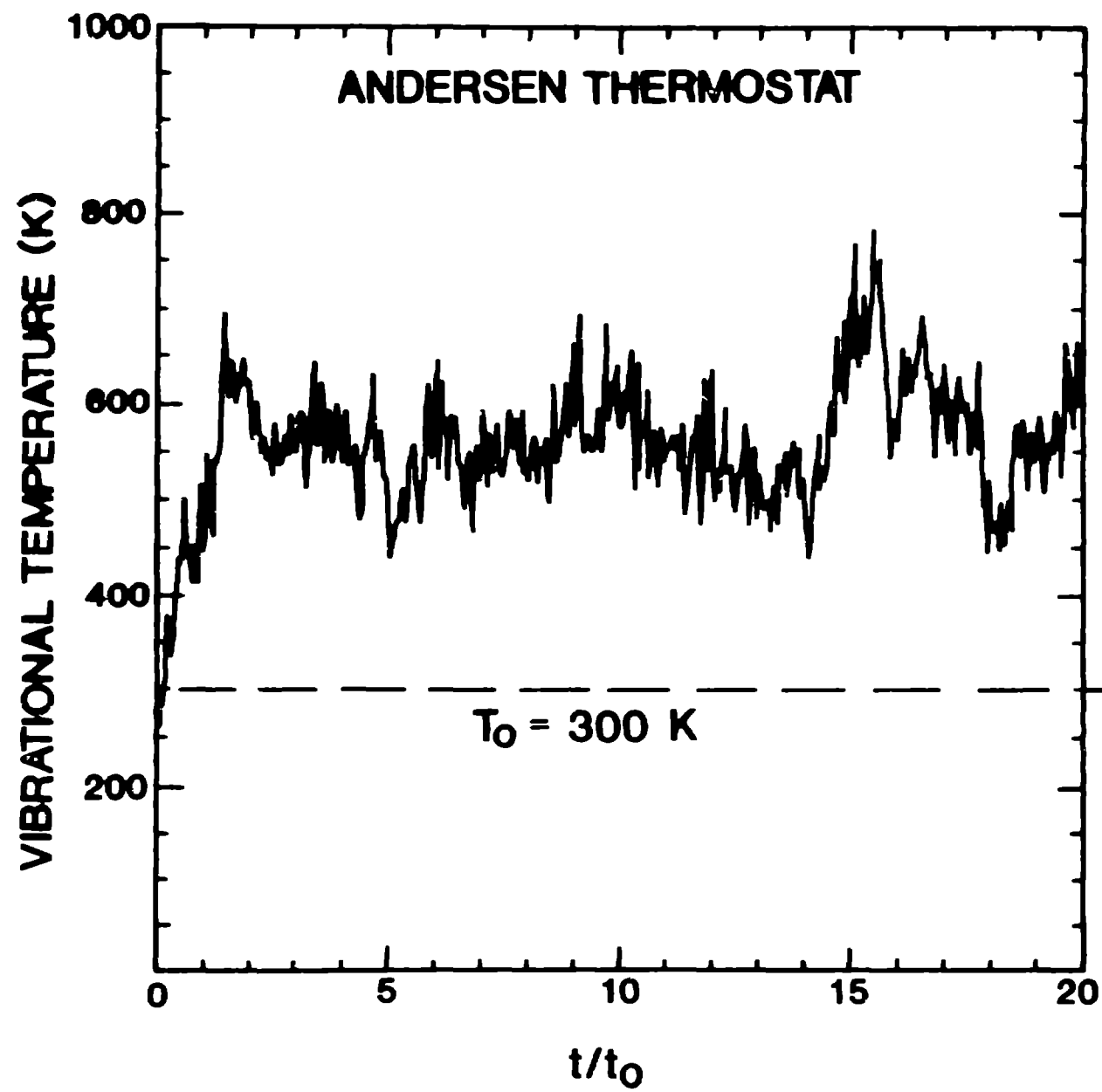


Fig. 6

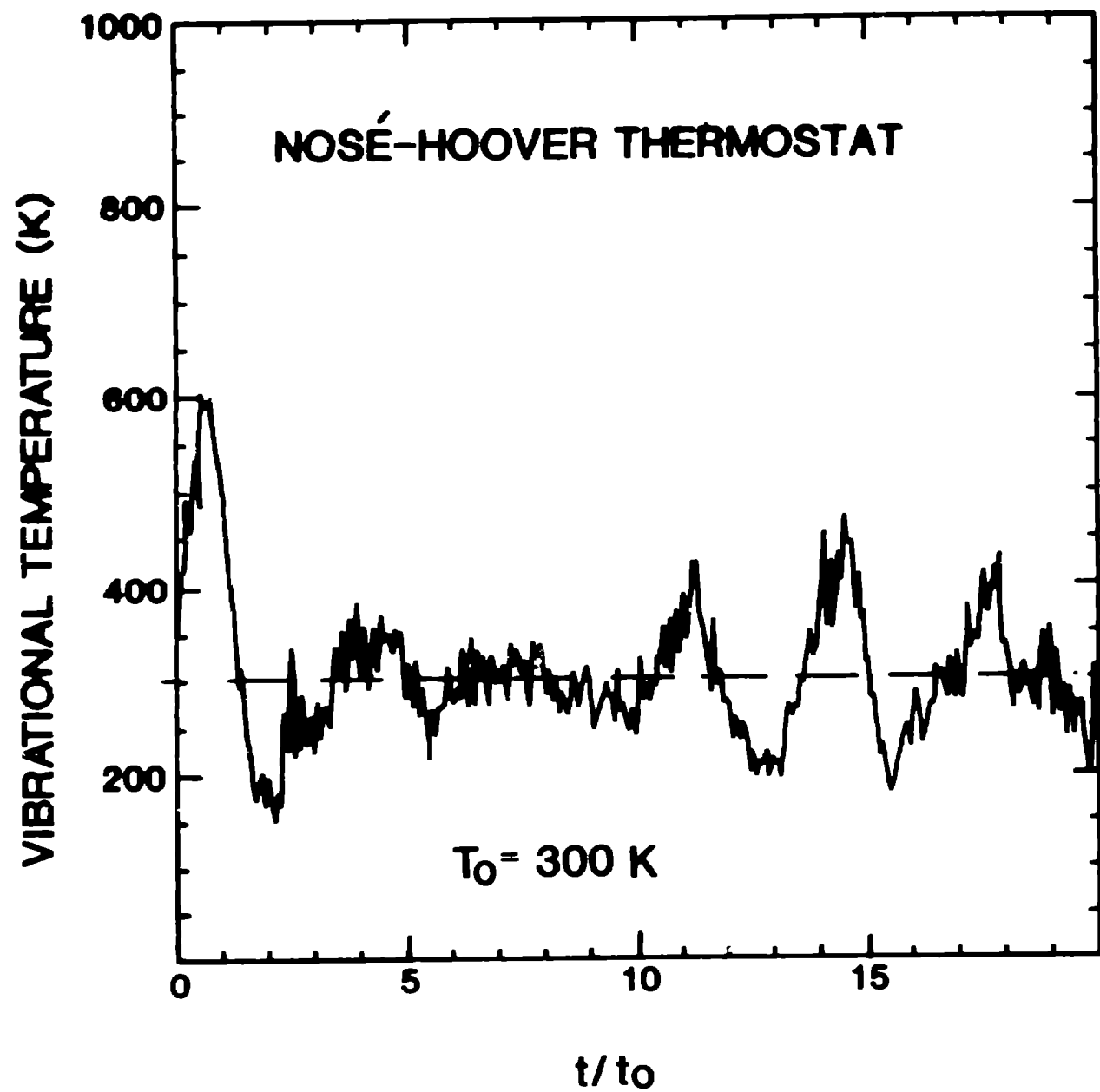


FIG. 7

